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► **To cite this version:**

C Dereumeaux, Fabien Mercier, P Soulard, C Fillol, P. Quenel, et al.. Assessing pesticides exposures for residents living close to vineyards in France. ISES 2000, Sep 2020, California Los Angeles, United States. hal-04936913

HAL Id: hal-04936913

<https://hal.science/hal-04936913v1>

Submitted on 9 Feb 2025

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Assessing pesticides exposures for residents living close to vineyards in France



Background

Residents living close to vineyards might be exposed to pesticides through non-occupational pathways including spray drift and volatilization of pesticides beyond the treated area. The aim of our study was to identify relevant exposure biomarkers for pesticides specifically used in vineyards, and to compare biomarker distributions between residents living close to vineyards and controls.

Materials and methods

Study population

The study population was based on a selection of 60 adults and 60 children, selected from of a national cross sectional survey (Esteban study) based on a representative sample (2,503 adults 18-74 y.o and 1,104 children 6-17 y.o) of the French population conducted between 2014-2016. It included 30 adults and 30 children living within 500 meters of vineyards and 30 adults and 30 children living at 2 kilometers or more of vineyards.

Biomarkers measurements

An exhaustive list of pesticides used specifically in treated vineyards was built. These pesticides were prioritized considering their application frequencies, physicochemical properties, and intrinsic toxicity. Then we analyzed scientific literature to identify the biomarkers of exposure to the prioritized pesticides in urine and hair. We considered the biomarkers characteristics (half-life in urine and hair, specificity) and the analytical feasibilities (conditions for collection and storage, availability of an assay method) to finally select the most appropriate biomarkers.

Biomarkers of exposure to folpel (phthalimide and phthalic acid), mancozeb / metiram (ethylene thiourea [ETU] and ethylene urea [EU]), tebuconazole (tebuconazole and hydroxytebuconazole [TEB-OH]), captan (tetrahydrophthalimide [THPI]), and boscalid (boscalid) were measured in urine samples collected among the study population.

Phthalimide, phthalic acid, tebuconazole, TEB-OH, THPI and boscalid were analyzed by gas chromatography coupled to tandem mass spectrometry (GC/MS/MS) after a solid phase extraction (SPE) step followed by a derivatization procedure (silylation). ETU and EU were also analyzed by GC/MS/MS after a supported liquid extraction (SLE) step followed by the same derivatization procedure. Limits of detection (LOD) and limits of quantification (LOQ) are given in table 1.

Table 1 | LOD and LOQ of biomarkers of exposure to folpel, mancozeb / metiram, tebuconazole, captan and boscalid in urine

	LOD (µg/L)	LOQ (µg/L)
Phthalic acid	2.5	5.0
Phthalimide	0.5	1
Tebuconazole	1.3	2.5
TEB-OH	1.3	2.5
THPI	1.3	2.5
Boscalid	1.3	2.5
ETU	0.4	1
EU	0.2	0.5

Statistical analysis

For each biomarker, descriptive statistics were run for adults and children. Each value below LOD was replaced by a value between 0 and the LOD which was randomly generated, assuming a log-normal distribution. Values below the LOQ and above the LOD were taken into account. If the proportion of results above the LOD was lower than 40%, geometric means (GM) were not calculated. If the percentile estimate was under the LOD or LOQ, the percentile was not reported and was denoted, respectively, as “<LOD” or “<LOQ”.

We test whether log-transformed urinary metabolite levels differed between residents living close to vineyards and controls using t-test. Tests were performed when the proportion of detected samples was above 40%.

All the analyses were performed for adults and children separately. The statistical analyses were conducted using SAS Enterprise Guide 7.1.

Results

Urinary pesticide concentrations in the study population

Phthalic acid was detected in all urinary samples, whereas phthalimide, ETU and EU were detected in nearly one sample in two and TEB-OH was detected in one sample in three for adults. Tebuconazole, THPI and boscalid were never detected in urinary samples. Distributions (GM and percentiles) of biomarkers levels are given in table 2 (adults) and table 3 (children).

Table 2 | Urinary levels of biomarkers of exposure to folpel, mancozeb / metiram, tebuconazole, captan and boscalid in adults (µg/L)

Biomarker	N	%>LOD	GM [CI 95%]	P25	P50	P75	P90	P95	Max
Phthalic acid	60	100%	60.0 [46.2 – 77.8]	27.5	55.0	129.5	201.0	288.2	1,281.8
Phthalimide	60	48%	0.7 [0.6 – 0.9]	<LOD	<LOQ	1.2	1.7	2.4	7.4
ETU	60	47%	0.4 [0.3 – 0.5]	<LOD	<LOQ	<LOQ	1.2	2.3	5.9
EU	60	63%	0.3 [0.2 – 0.5]	<LOD	<LOQ	0.7	1.9	3.1	5.6
TEB-OH	60	37%	NC	<LOD	<LOD	<LOQ	5.7	7.2	18.7
Tebuconazole	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
THPI	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Boscalid	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 3 | Urinary levels of biomarkers of exposure to folpel, mancozeb / metiram, tebuconazole, captan and boscalid, in children (µg/L)

Biomarker	N	%>LOD	GM [CI 95%]	P25	P50	P75	P90	P95	Max
Phthalic acid	60	100%	43.7 [35.7 – 53.5]	27.8	38.6	62.4	113.0	211.5	479.3
Phthalimide	60	48%	0.6 [0.5 – 0.7]	<LOD	<LOQ	<LOQ	1.1	1.3	2.0
ETU	60	47%	0.4 [0.3 – 0.5]	<LOD	<LOD	<LOQ	1.2	2.3	4.3
EU	60	53%	0.2 [0.1 – 0.3]	<LOD	<LOQ	<LOQ	0.6	0.7	2.6
TEB-OH	60	7%	NC	<LOD	<LOD	<LOD	<LOQ	<LOQ	3.9
Tebuconazole	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
THPI	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Boscalid	60	0%	NC	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Comparisons between residents living close to vineyards and controls

Considering the proportion of samples below the LOD, comparisons between residents living close to vineyards and controls were not conducted for boscalid, tebuconazole, TEB-OH and THPI. T-test results are presented in figure 1 (adults) and 2 (children).

The comparisons only showed slight difference between phthalimide urinary levels for children living close to vineyards and controls. No other difference was observed in the study population.

Figure 1 | Comparisons of folpel and metiram / mancozeb biomarkers levels between residents living near vineyards and controls (adults)

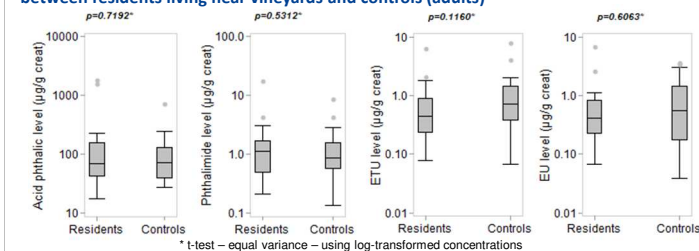
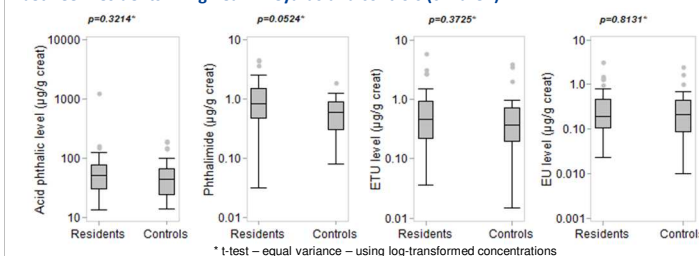


Figure 2 | Comparisons of folpel and metiram / mancozeb biomarkers levels between residents living near vineyards and controls (children)



Discussion / Conclusion

These preliminary results showed that biomarkers of folpel and metiram / mancozeb were frequently detected in urinary samples collected in the Esteban study. However, only phthalimide urinary levels were slightly higher in children living close to vineyards in comparison with controls. Some study design characteristics (small population, seasonal variation of the urine collection) may explain these results, as the Esteban study was not designed to accurately measure pesticide spray-drift exposure in residents living close to vineyards.

The main determinants of levels of biomarkers of folpel and metiram / mancozeb will supplement these preliminary results, as well as biomarkers measurements in hair. These results will be useful to define the best biomarker-matrix pairings and highlight requirements for future epidemiological studies in order to accurately measure pesticide spray-drift exposure in residents living close to vineyards.

Acknowledgments

The authors received no financial support for the research, authorship, and/or publication of this poster. The authors have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter discussed in this poster.